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Beneficial transitions in thermogravimetric signals and activation energy levels due to briquetting of raw pigeon pea stalk

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HIGHLIGHTS

- Thermal hardness of briquette was established over raw biomaterial.
- TG-signals transitions from briquette to raw bio-material were explained.
- Distinct hydrogen TG-signal in briquetted biofuel.
- Methane TG-signals in raw pigeon pea stalk.
- Briquette showed higher activation energies (KAS method) over raw pigeon pea stalk.

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ABSTRACT

Transitions of thermogravimetric signals beneficial for formation of the binder-less briquetted biofuel of pigeon pea crop residues were investigated. Thermal hardening or softening of the different components of bio-material in briquetted biofuel was explained in terms of transitions of thermogravimetric signals and activation energy levels. The activation energy profiles with respect to conversion fraction for raw residue and its briquette was studied by Kissinger–Akahira–Sunose method. The activation energy profile of briquette showed dominancy over raw residues of pigeon pea crop highlighting the overall hardening in briquetted biofuel.

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1. Introduction

Briquette is compact solid fuel made from the loose biomass [1–3]. The formation of briquettes is attractive for better utilization of loose crop residues (CR) for energy generation [4,5]. The crop residues are available in a substantial quantity after the harvest of the crop [6] which can be used as a sustainable renewable energy source. Most of the crop residues are not suitable for energy generation [1–3] in energy gadgets due to their low bulk density <200 kg/m^3. The low bulk density creates problem in handling, transportation and storage of crop residues. Due to less density, the energy density of crop residues is low. Also, CR requires a lot of space for the transportation. Briquetting [1–3] is densification process of biomass to produce uniformly sized solid pieces of high density, which can be conveniently used as fuel. Briquettes can be produced from the loose biomass until the density of 1200 kg/m^3 [7]. The uniformly sized compact biofuel shows better flow ability in bio-reactors for getting better performance of energy gadgets. In India, briquettes are mostly produced from saw dust, bagasse, mustard stalk, ground nut shell, cotton stalk mix with press mud.

Pigeon pea stalk (PPS) is crop residues. In developing countries, many times, farmers burn crop residues in open fields, to clear their fields for next sowing, which is detrimental to environment, and also is loss of a potential energy resource [8]. The pigeon pea stalk can be collected and converted in briquetted solid biofuel for substituting the use of fire wood in thermal devices such as furnaces and boilers. In context of farmer's perspective, the residues of pigeon pea crop are just like wastage bio-materials which do not give financial gains to them. Even, they need to spend the money to clean the fields from crop residues. Farmers can obtain substantial economical gains if they sell the briquetted biofuel. Considering the production cost (all expenses starting from biomass harvesting, collection, transportation to the production of briquettes), the farmers can obtain 20–30% profit over the

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investment made. Tripathi et al. evaluated the techno-economics of biomass briquetting in India [1]. Sengar et al. highlighted the economic feasibility of briquetted fuel [9].

Basically, almost all lignocellulosic crop residues can be briquetted by changing the process parameters of the briquetting [10,11]. There are different types of commercially available briquetting machines. Mainly, three types of briquetting systems are used for production of briquettes which are: (i) Screw-press type, (ii) Piston-press (die-punch) type and (iii) Rotary dies and roller type [1–3,5].

In piston-press type systems, raw bio-material is pressed by the piston (ram) through a die, putting very heavy pressure to heat and press raw bio-material to form briquettes. In screw press type briquetting machine, a conveyer screw conveys raw material to the die to exert heavy pressure on raw bio-material. The die in the screw press type systems are an opening to allow extruded and densified briquettes, to come out of the machine. The piston-press machines exert pressure in regular pulses and screw-press systems exert pressure continuously. At present, both types of system are in use. Piston-press type system consumes less energy per unit output [1–3,5].

Briquetting process can be done using some binder [12] or without binder. Use of binders increases the cost of production of the briquettes. Teixeira et al. presented the work on hand pressed briquettes using charcoal mixed with a binder (starch) obtained from cassava flour (a tropical root) [13]. The present article is dedicated to TG-analysis highlighting the transitions for binder-less briquette produced by piston press machine. In binder-less briquetting the lignin of raw material itself acts as binder. The lignin acts as binder after experiencing the changes in its configurations as compared to lignin's configuration in the raw bio-material. The information of transitions in polymeric bio-constituents is useful for selecting the operational parameters of briquetting machine, and also to foresee the future design refinements in briquetting press.

Binder-less briquetting process needs high pressure and temperature as compared to the briquetting with binder. Lignocellulosic bio-materials can be briquetted without binder. Cellulose, hemicellulose, lignin are the main components of crop residues. In briquetting, the raw bio-material is compressed at pressures as high as 100 MPa [7] and temperatures exceed 200 °C in the die-region to soften the lignin which fuses the biomass particles into briquettes or pellets of desired shape and size [2,3]. Lignin acts like a binding agent. This is basically a change in the bio-matrix due to high pressure and temperature exerted on the bio-material. This can be investigated in-depth using the thermogravimetric analysis (TGA) wherein a bio-material is subjected to heat in precisely monitored chamber. Thermal decomposition of bio-materials can be assumed to occur in the stages of moisture release, hemicellulose decomposition, cellulose decomposition and lignin decomposition as stated by Vasile et al. [14]. Caballero et al. [15] and López-González et al. [16], explained the thermal decomposition of lignocellulosic bio-materials as the summation of independent decompositions of their main components. Ledakowicz and Stolarek informed that the evolution of each volatile can be considered as a single first order reaction assuming that the constituents of bio-material are evolved by independent parallel reactions [17]. According to Sanchez-Silva et al., hemicellulose has a random and amorphous structure with little strength whereas cellulose has a crystalline and strong structure [18]. They also mentioned that lignin showed the highest thermal stability, decomposing in the whole range of temperatures studied (200–700 °C) and the DTG profile of lignin was the flattest [18]. Decomposition of lignin is very difficult as it is heavily cross-linked highly branched complex polymer.

Present article is the first writing, presenting the comparative thermogravimetric kinetics of pigeon pea crop residue and its briquette (PPB). The thermal hardening or weakening of various specific bio-components was discussed and explained. Established methods for determination of kinetics [19–21] of thermal decomposition are Friedman, Coats–Redfern, Kissinger–Akahira–Sunose (KAS), and Ozawa–Flynn–wall (OFW). Coats–Redfern, Kissinger–Akahira–Sunose (KAS) and Ozawa–Flynn–wall are integral iso-conversional method whereas Friedman method is differential method [21]. In different methods like Friedman or KAS or OFW or Coats–Redfern, there is need to extract the points from TGA data to draw the iso-conversional kinetic lines at selected conversional fractions. The x and y coordinates of Coats–Redfern, Friedman, KAS, OFW points are $(1/T, \ln(-\ln(1-\alpha)/T^2)$, $(1/T, \ln(d\alpha/dt))$, $(1/T, \ln(\beta/T^2))$ and $(1/T, \ln(\beta))$, respectively. The slopes of kinetic lines, $\ln(-\ln(1-\alpha)/T^2)$ versus $1/T$ (in modified Coats–Redfern method), $\ln(d\alpha/dt)$ versus $1/T$ (in Friedman method), $\ln(\beta/T^2)$ versus $1/T$ (in KAS method) and $\ln(\beta)$ versus $1/T$ (in OFW method) gives the estimate of $-E/R$. The Coats–Redfern method is good to find the kinetics at a single heating rate as stated by White et al. [19]. As the temperature is independent variable in thermogravimetry, the temperature based method serve as better options to determine the kinetics. With an ability to consider effect of heating rates, the KAS method was taken as appropriate method in this article.

In present article, transitions of thermogravimetric signals occurring due to briquetting are explained on the basis of activation energy profiles of PPS and PPB. The superior activation energy profile of the PPB was obtained.

2. Materials and methods

The residue of pigeon pea crop (PPS) was taken for study. Thermogravimetric analyses (TGA) of powdered PPS and its briquettes were done to understand the internal changes in the configuration and thermal stability of the different bio-components.

The samples of raw PPS for TGA were powdered having the particle distribution of as particle size >0.2 mm (5–6%), 0.2–0.4 mm (6–7%), 0.4–0.7 (18–20%), 0.70–1.4 mm (19–20%), 1.4–1.7 mm (22–23%) and <1.7 mm (27–28%). For making briquettes, powdered PS was briquetted using a commercial piston-press type biomass briquetting machine (rated capacity 500 kg/h; rated power 35 kW). The briquetting plant (installed at Agricultural Energy and Power Division, Central Institute of Agricultural Engineering, Bhopal, India) is shown in earlier writing [22]. The powdered PPS was fed to briquetting machine exerted heavy pressure (>100 MPa) on raw powdery PPS to form PPB. The temperatures at the die of briquetting machine reached above 200 °C. Thus, during the briquetting the PPB underwent through stresses due to high temperature and pressure in a semi-confined environment. The moisture contents of powdered PPS and PPB were 8–12% (dry weight basis). Ash contents of samples of the PPB and PPS were 4% and 1%, respectively. The bulk densities of powdered PPS and PPB were near 250–270 and 640–650 kg/m^3, respectively. It was densification of the level of 2–3 times due to briquetting. The true densities of briquettes were 1140–1160 kg/m^3. The elemental composition of briquettes (PPB) of pigeon pea crop residues showed the presence of C, H, N and S as 43.0, 6.5, 1.0 and 0.5%, respectively.

Thermogravimetric analyzer (Model: pyris-6; Make: Perkin Elmer) was used. For TG-analysis, same heating method was decided for both types of bio-materials. The temperature of TGA was first maintained at 35 °C for 2 min and then, it was raised (at different heating rates (β)) to the temperature of 1000 °C in Argon inert environment. Four β (10, 20, 30 and 40 °C/min) were used. Kissinger–Akahira–Sunose (KAS) [19–21] method was used for kinetic analysis in relation to conversion fraction (α) using following Eq. (1):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) - \ln g(\alpha) - \frac{E}{RT} \tag{1}$$

$$g(\alpha) = \int_{\alpha i}^{\alpha o} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \int_{Ti}^{To} e^{\left(-\frac{E}{RT}\right)} \cdot dT \tag{2}$$

$$\alpha = \frac{wi - wt}{wo - wf} \tag{3}$$

where E is the activation energy; A is Arrhenius pre-exponential factor; R is Universal gas constant; T is reaction temperature (absolute); Ti is reaction temperature at initiation; To is temperature at the αo; αi is conversion fraction at initiation; αo is conversion fraction at To; and $f(\alpha)$ is the reaction model. The wi, wt and wf are the masses of bio-material at initial, instantaneous and final stages of decomposition, respectively.

In KAS method, iso-conversional kinetics are determined assuming the terms, ln $g(\alpha)$ and ln A as constant at a specific value of α in Eq. (1). Thus, Eq. (1) takes a form of linear equation with its slope equal to $-E/R$. For complete model treatment on TG-data, the full range of conversion fraction (0–1) was divided at twenty three α-values such as 0, 0.01, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 0.99 and 1.00 for executing kinetics computations.

3. Results and discussion

Differential thermogram (DTG) of PPS and PPB are given in Figs. 1–5 showing the region of moisture release, hemicellulose, cellulose, lignin, and methane or hydrogen, respectively, with respect to temperature (T-domain) and conversion fraction (α-domain). The decomposition rates are negative as the weight is reduced during the thermogravimetric analysis in all figures.

3.1. Analysis of transitions of thermogravimetric signals due to briquetting

The region 50–200 °C (Fig. 1) was related with the dehydration. In PPS, the moisture related signals showed their presence until 190 °C whereas in PPB, this signal existed until 210 °C. The moisture peaks shifted to higher temperature region with increase in β for PPS and PPB. On comparison of the moisture peaks, the locations of moisture related peak in PPB were at higher temperatures than their corresponding locations in the PPS (Fig. 1). It indicated the thermal strengthening of the moisture due to briquetting. Due to heating during the briquetting process, the surface moisture of the particles of PPS escaped and the residual moisture in PPB remained as the internally bound moisture. With respect to conversion fraction (Fig. 1), the transitions in locations of moisture signals were towards higher α-value in PPB with respect to PPS at all β showing hardening effects. The transitions in amplitudes of moisture signals towards lower decomposition rate in PPB in reference to PPS at β of 10, 20 and 30 °C/min showing thermal stability of moisture in PPB. At 40 °C/min, the PPB related rate in moisture region exceeded over the PPS. This showed that in PPB, there existed internally bound moisture which could be extracted only at higher β.

The hemicellulosic [23–28] decomposition TG-signals were seen in the region of 220–320 °C in (Fig. 2) PPS and PPB. The hemicellulosic decomposition rates were lower than cellulosic decomposition. This is a similar finding as given by Shen et al. [23]. TG-signals were almost similar at β of 10 and 20 °C/min in both bio-materials, temperature-wise and α-wise. However, the amplitude of TG-signal was slightly lower in PPB as compared to PPS at 10 °C/min indicating thermal hardening. The locations of hemicellulose were at higher temperature in PPB at heating rate of 30 and 40 °C/min showing thermal hardening. But the decomposition rates were also higher in PPB at 30 and 40 °C/min showing thermogravimetric softening. However, hemicellulosic transitions could not infer logical conclusions.

Cellulosic [23–28] thermogravimetric signals (Fig. 3) made their transitions (in the range of 320–380 °C) towards thermal hardening. The locations of these signals were at higher temperature in PPB as compared to PPS at all β. Also, decomposition rates were low in PPB as compared to PPS. The cellulosic region was spread in α-span of 0.4–0.8 in PPS and 0.4–0.82 in PPB. Transitions of

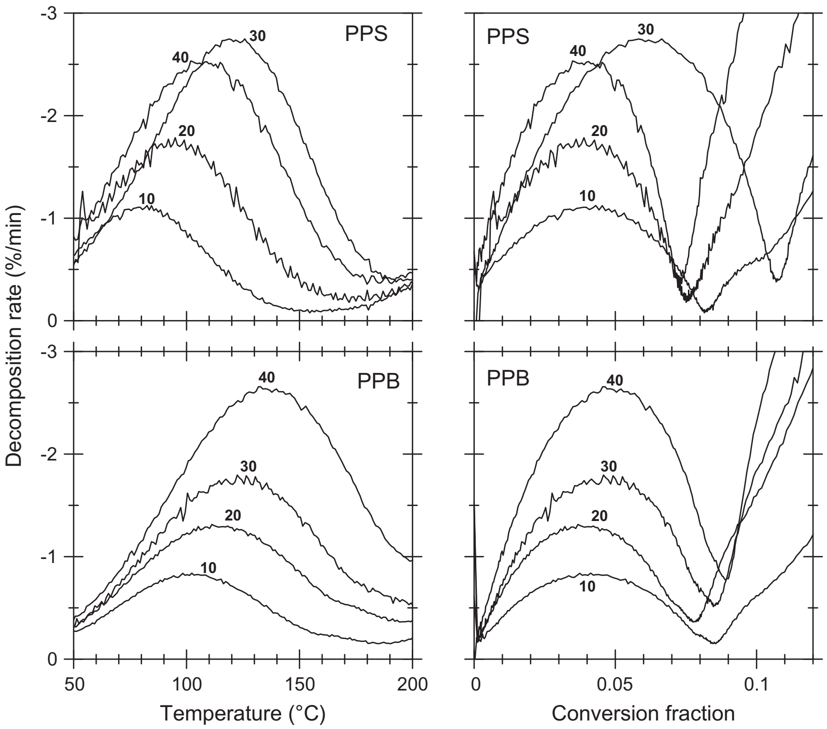

Fig. 1. Transitions of moisture TG-signals from PPS to PPB. (Numbers 10, 20, 30 and 40 are heating rates (°C/min) at which that particular TG-curve was obtained).

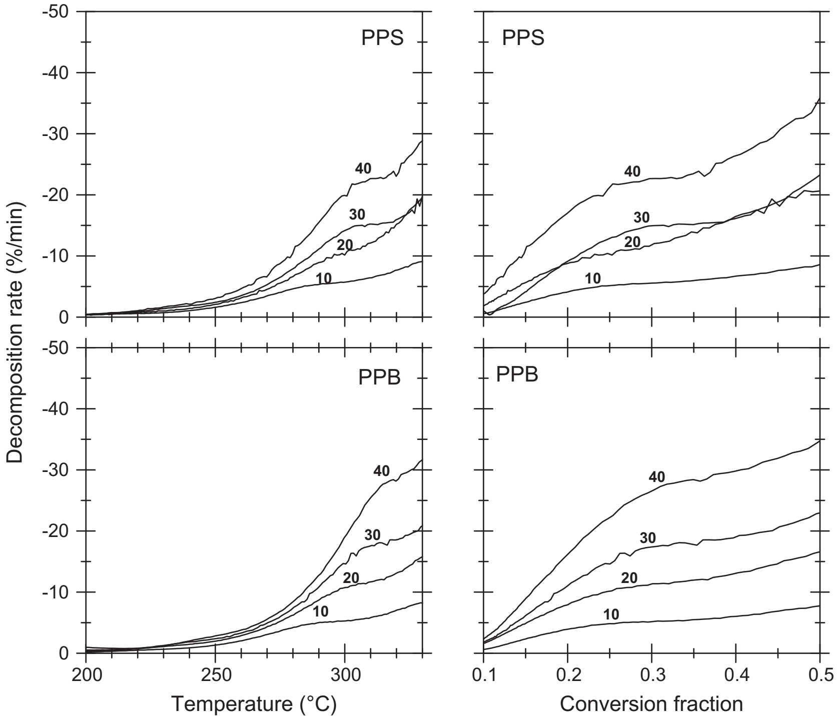

Fig. 2. Transitions of hemicellulose TG-signals from PPS to PPB. (Numbers 10, 20, 30 and 40 are heating rates (°C/min) at which that particular TG-curve was obtained).

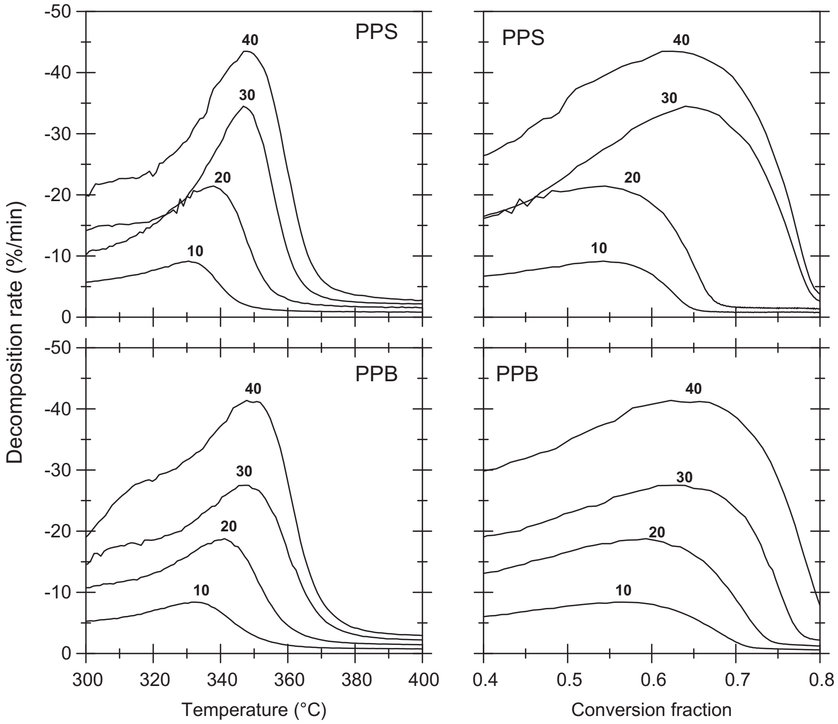

Fig. 3. Cellulose related transitions from PPS to PPB. (Numbers 10, 20, 30 and 40 are heating rates (°C/min) at which that particular TG-curve was obtained).

TG-signals in α-domain were similar as seen in temperature domain. According to López-González et al., during cellulosic decomposition, a complex set of reactions as denitration and deacetylation, scission of O–N, C–O, CC and C–H bonds might take place [16]. During hemicellulose decomposition, the breakdown of C–O–C and some pyranose C–C bonds is possible [16]. Vasile et al. [14] indicated that hydrocarbons, aldehydes, ketones, acids, alcohols and others are generated by the primary pyrolysis of hemicelluloses and cellulose in single stages, occurring within the 290–400 °C region.

The lignin related thermogravimetric signals [25–28] were observed near the temperature 500 °C (Fig. 4) in both bio-materials. The lignin decomposition is expected to impact a three-dimensional structure consisting of phenylpropane coupled with C–C or

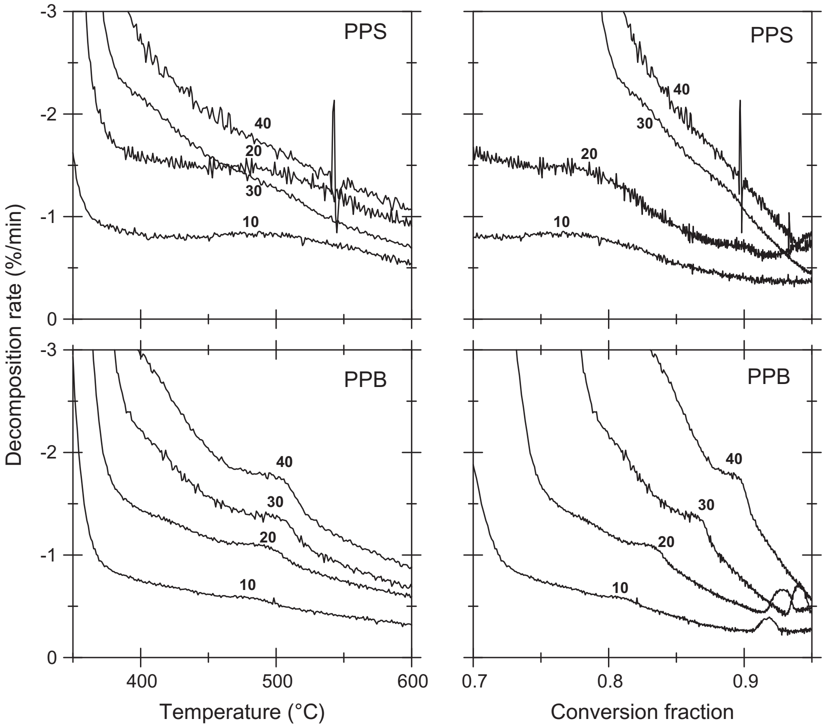

Fig. 4. Transitions of lignin TG-signals from PPS to PPB. (Numbers 10, 20, 30 and 40 are heating rates (°C/min) at which that particular TG-curve was obtained).

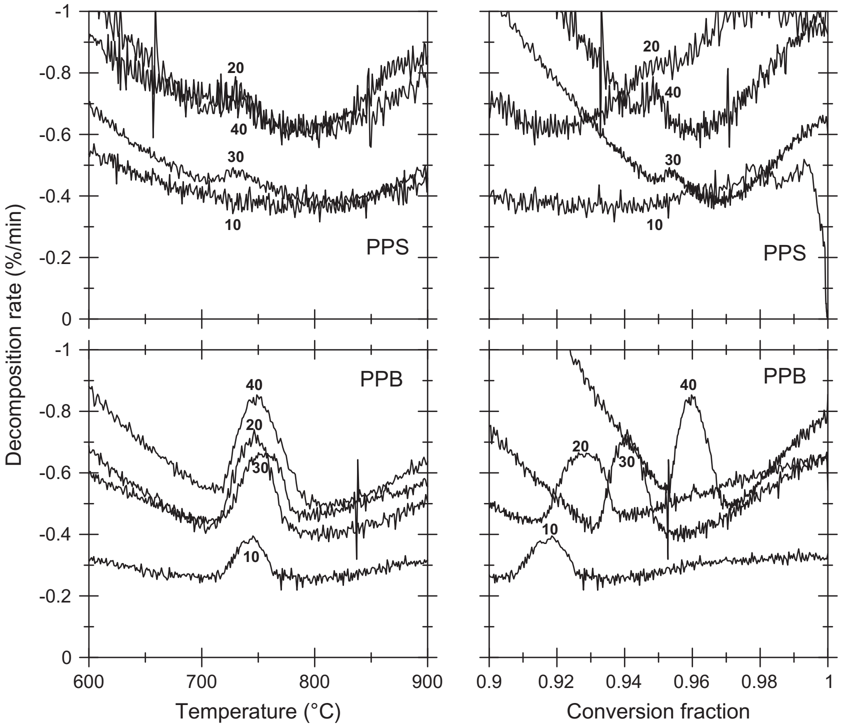

Fig. 5. Transitions of methane and hydrogen related TG-signals in PPS and PPB, respectively. (Numbers 10, 20, 30 and 40 are heating rates (°C/min) at which that particular TG-curve was obtained).

C–O–C bonds whose activity covers a wide range of temperatures as suggested by López-González et al. [16]. They also added that phenols and alcohols are the dominant volatiles released from lignin pyrolysis in two successive stages, the main one appearing at temperatures over 500 °C [16]. The lignin related transitions were seen in the α-range of 0.7–0.8 in PPS. The signals in PPS were broad, flat and dull. In PPB, the lignin showed its clear presence in α-span 0.75–0.92. The shift related to lignin TG-signals towards the higher α can be noticed for PPB indicating thermal hardening. The lignin decomposition rate was lower at 10 and 20 °C/min and higher at 30 and 40 °C/min in PPB in comparison to PPS in T-domain as well as in α-domain. This article considered that the lignin in PPS first

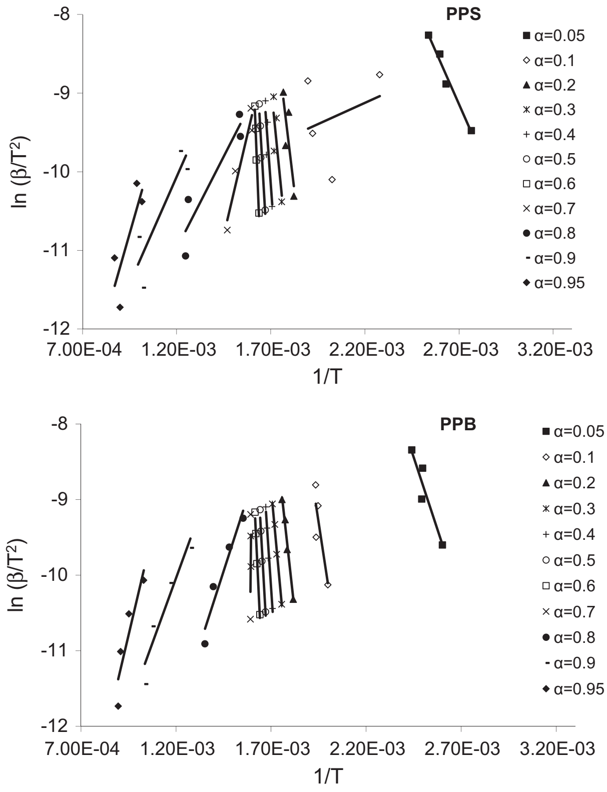

Fig. 6. KAS kinetics lines for PPS and PPB.

relaxed, then melted during briquetting, and finally solidified in PPB. The solidification of melted lignin was the probable cause of strengthening in PPB.

The peaks near the 750 °C (Fig. 5) in PPB were seen and ascribed to the hydrogen release due to charring process. Idris et al. [29] obtained TG-signals at higher temperature (650–750 °C) for lignocellulosic palm kernel shell under pyrolysis conditions. They ascribed peaks in the range of 700–750 °C to presence of methane and release of hydrogen [29]. The peaks at higher temperature near 750 °C was related to hydrogen release and peaks falling at relatively lower temperature 700–730 °C were linked with the presence of methane [29]. The results of present article showed that in PPB the hydrogen release was prominent and in PPS, the dull peaks were related to methane were noticed. These signals were located at α-value of 0.92, 0.93, 0.94 and 0.96 at β of 10, 20, 30 and 40 °C/min, respectively, in PPB. In PPS, the methane TG-signals could not be identified properly at 10 and 20 °C/min. However, at 30 and 40 °C/min minor signals were seen near α-value of 0.95. In PPS, the methane TG-signals was just after and just prior to α-value of 0.95 at 30 and 40 °C/min, respectively. There was tendency of shifting of methane signals towards lower α-value with increase in β in PPS. The hydrogen signals in the PPB were sharper than methane signals in PPS. In general, the locations of hydrogen TG-signals in PPB shifted towards higher temperature with increase in β.

3.2. Kinetics

The, $\ln(\beta/T^2)$ versus $1/T$, KAS-curves were drawn for thermal decomposition at all experimented β for both bio-materials. The iso-conversional points were taken in complete conversion range ($\alpha = 0$–1) at selected α-values of 0, 0.01, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 0.99 and 1.00. The activation energy profiles with respect to α for PPS and PPB were arrived by plotting the KAS kinetic lines. For this, KAS points ($1/T$, $\ln(\beta/T^2)$) were extracted from KAS-curves (taken at all experimented β) at selected α. The plots of KAS kinetics lines, i.e., $\ln(\beta/T^2)$ versus $1/T$, at different α-values are given in Fig. 6 for PPS and PPB. Table 1 shows equations of the linear KAS lines at different α-values for PPS and PPB. The cut-off of R^2 to compute the activation energy using KAS kinetics lines was considered adequate $\geqslant 0.8$ for comparative studies. Activation energy for few α-points was not computed as shown in Table 1. Table 2

Table 1

Linear correlation equations for KAS iso-conversional lines ($\ln(\beta/T^2)$ versus $1/T$) for PPS and PPB.

α	Pigeon pea stalk (PPS)			Briquette (PPB)		
	Equation of linear fitting for KAS points	R^2		Equation of linear fitting for KAS points	R^2	
0	$y = 66446x - 221.85$	0.4053	×	$y = -42834x + 129.05$	0.0867	×
0.01	$y = -9079.3x + 18.862$	0.9771	√	$y = -11703x + 25.609$	0.9479	√
0.05	$y = -5434x + 5.5305$	0.9748	√	$y = -7661x + 10.334$	0.8897	√
0.10	$y = 1082.2x - 11.505$	0.0904	×	$y = -16510x + 22.893$	0.7365	×
0.15	$y = -10937x + 10.639$	0.3859	×	$y = -21889x + 30.555$	0.9681	√
0.20	$y = -19887x + 26.075$	0.6926	×	$y = -22935x + 31.351$	0.9862	√
0.25	$y = -23691x + 32.085$	0.72	×	$y = -24892x + 34.048$	0.9878	√
0.30	$y = -24343x + 32.514$	0.6889	×	$y = -27445x + 37.808$	0.991	√
0.35	$y = -29042x + 39.934$	0.7435	×	$y = -31630x + 44.338$	0.9764	√
0.40	$y = -33269x + 46.406$	0.7865	×	$y = -37203x + 53.076$	0.9755	√
0.45	$y = -36669x + 51.393$	0.8897	√	$y = -40459x + 57.805$	0.9831	√
0.50	$y = -40915x + 57.829$	0.9217	√	$y = -45125x + 64.886$	0.968	√
0.55	$y = -46543x + 66.441$	0.9335	√	$y = -43685x + 61.867$	0.9555	√
0.60	$y = -61059x + 89.452$	0.9583	√	$y = -52469x + 75.548$	0.9803	√
0.65	$y = 84145x - 144.72$	0.7188	×	$y = -64465x + 94.185$	0.9601	√
0.70	$y = 10205x - 25.612$	0.9233	√	$y = 268880x - 438.16$	0.3009	×
0.75	$y = 5586.6x - 18.183$	0.8774	√	$y = 14929x - 32.857$	0.9923	√
0.80	$y = 4673.9x - 16.586$	0.8713	√	$y = 7787.8x - 21.243$	0.9331	√
0.85	$y = 4982.1x - 16.575$	0.8414	√	$y = 7084.2x - 19.468$	0.9208	√
0.90	$y = 5432.7x - 16.586$	0.7952	×	$y = 6911.8x - 18.334$	0.9075	√
0.95	$y = 8392.7x - 18.761$	0.6685	×	$y = 10733x - 20.992$	0.8281	√
0.99	$y = -1167.8x - 10.142$	0.0003	×	$y = 54131x - 55.58$	0.7803	×
1.00	$y = 173433x - 149.69$	0.9722	√	$y = 147142x - 128.75$	0.9299	√

Where $y = \ln(\beta/T^2)$ and $x = 1/T$.
The cut-off value of R^2 for performing further KAS analysis was 0.8.
× infers the KAS analysis inadequate for determination of kinetics.
√ infers the KAS analysis adequate for determination of kinetics.

Table 2
Activation energies for PPS and PPB calculated using slope of KAS iso-conversional lines ($\ln(\beta/T^2)$ versus $1/T$).

α	Activation energy (kJ/mol)	
	Pigeon pea stalk (PPS)	Briquette (PPB)
0.01	75	97
0.05	45	64
0.10	–	–
0.15	–	182
0.20	–	191
0.25	–	207
0.30	–	228
0.35	–	263
0.40	–	309
0.45	305	336
0.50	340	375
0.55	387	363
0.60	508	436
0.65	–	536
0.70	85	–
0.75	46	124
0.80	39	65
0.85	41	59
0.90	–	57
0.95	–	89

shows the α-dependent variations in activation energy for both bio-materials. In general, activation energy profile of the PPB was found dominating over PPS showing thermal hardening. The activation energies are the energies required to excite the bio-material or bio-constituents at particular temperature. While designing a system to utilize the bio-material for energy generation, one can precisely find the initial energy input needed to start the thermal decomposition of bio-material. Once, biofuel starts decomposing, the estimation of the energy output from biofuel is possible using activation energy values. As bio-materials have complex bio-matrix, the most complex bio-constituent can be used for simplicity to determine the energy required to initiate the thermal decay at a given temperature. Thus, the maximum initiation energy for decomposition of bulk bio-material can be found. For energy output, TG-activation energy levels are the maximum possible energy that may emerge using the biofuel. Practically, deliverable energy from biofuel may be less than TG-activation energy due to various losses during bulk matter decomposition.

4. Conclusions

Raw pigeon pea stalk and its briquetted biofuel were analyzed and compared using thermogravimetric analysis. Kinetics was evaluated using KAS method. Transitions of thermogravimetric signals occurring due to briquetting was discussed and explained. The activation energy profiles of raw residues of pigeon pea crop and its briquetted biofuel were compared to conclude that briquettes were thermally hard material to degrade than the raw crop residues.

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